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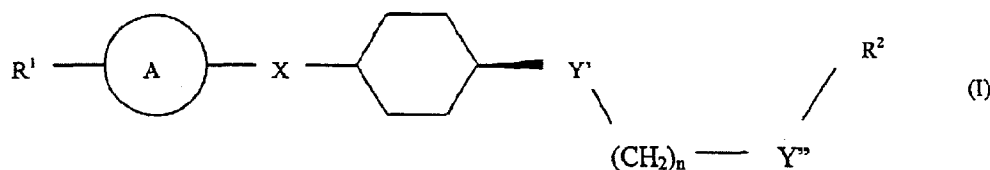
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(54) Title: LIQUID CRYSTAL COMPOUNDS



(57) Abstract: The use of a compound of formula (I) wherein R¹ is an alkyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R² is an alkyl or alkenyl group, Y' and Y'' are independently selected from oxygen or sulphur, n is an integer from 1 to 5, X is a direct bond or a C₁₋₄alkylene or C₂₋₄alkylene chain, and A is group comprising one or two rings which are independently selected from aryl, heterocyclic or cycloalkyl rings, and when there are two rings, they are bonded together directly or by way of a C₁₋₄alkylene or C₂₋₄alkylene group, for increasing the u.v. stability of a liquid crystal mixture. The compounds of formula (I) are u.v. stable and are useful in liquid crystal devices which are exposed to high levels of u.v. light such as phosphor display cells. Certain compounds are novel and these form a further aspect of the invention.

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Liquid Crystal Compounds

The present invention relates to liquid crystal mixtures which are stable to u.v. light, to liquid crystal devices containing these and to methods for increasing the u.v. stability of liquid crystal mixtures. Certain compounds useful in these mixtures are
5 novel and these, together with processes for their preparation, form a further aspect of the invention.

The term "liquid crystals" is well known. It refers to compounds which, as a result of their structure, will align themselves in a similar orientation, preferably at
10 working temperatures, for example of from -40 to 200°C. These materials are useful in various devices, in particular the liquid crystal display devices or LCDs. Liquid crystals can exist in various phases. In essence there are three different classes of liquid crystalline material, each possessing a characteristic molecular arrangement. These classes are nematic, chiral nematic (cholesteric) and smectic.

15 Broadly speaking, the molecules of nematic compounds will align themselves in a particular orientation in a bulk material. Smectic materials, in addition to being orientated in a similar way, will align themselves closely in layers.

A wide range of smectic phases exists, for example smectic A and smectic C. In the former, the molecules are aligned perpendicularly to a base or support, whilst in the
20 latter, molecules may be inclined to the support. Some liquid crystal materials possess a number of liquid crystal phases on varying the temperature. Others have just one phase. For example, a liquid crystal material may show the following phases on being cooled from the isotropic phase:- isotropic - nematic - smectic A - smectic C - solid. If a material is described as being smectic A then it means that the material possesses a smectic A
25 phase over a useful working temperature range.

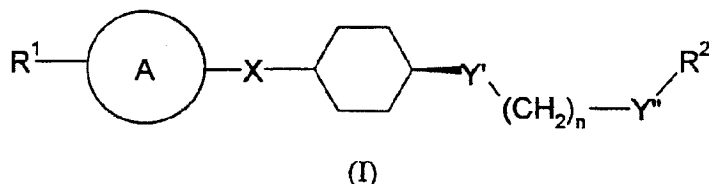
Such materials are useful, in particular in display devices where their ability to align themselves and to change their alignment under the influence of voltage, is used to impact on the path of polarised light, thus giving rise to liquid crystal displays. These are widely used in devices such as watches, calculators, display boards or hoardings,
30 computer screens, in particular laptop computer screens etc. The properties of the compounds which impact on the speed with which the compounds respond to voltage charges include molecule size, viscosity ($\Delta\eta$), dipole moments ($\Delta\epsilon$), conductivity etc.

In some cases however, the devices are subject to high levels of radiation such as ultra-violet radiation. Many liquid crystal compounds are not stable under these circumstances and can deteriorate rapidly.

Some examples of alkylene glycol liquid crystal compounds are found in EP-A-0385471 and JP-64-22835. EP-A-0824141 describes a complex series of liquid crystal mixtures, some of which may contain alkylene glycol compounds.

The applicants have found that certain of these structural types, as well as having useful liquid crystal properties, also have particularly good resistance to u.v. light, and so may be used to enhance the u.v. stability of liquid crystal mixtures.

The present invention provides the use of a compound of formula (I)

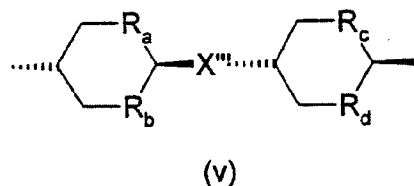
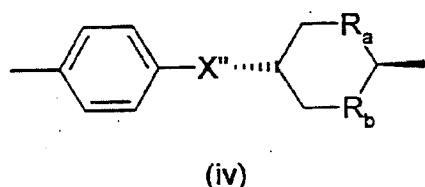
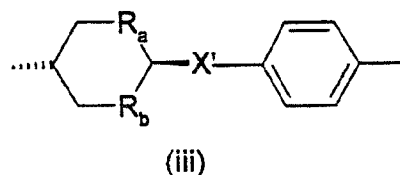
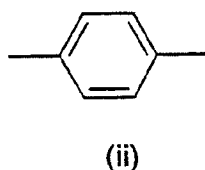
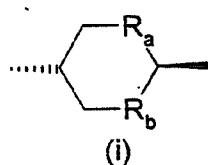


wherein R^1 is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R^2 is an alkyl or alkenyl group, Y' and Y'' are independently selected from oxygen or sulphur, n is an integer from 1 to 5, X is a direct bond or a C_{1-4} alkylene or C_{2-4} alkenylene chain, and A is group comprising one or two rings which are independently selected from aryl, heterocyclic or cycloalkyl rings, and when there are two rings, they are bonded together directly or by way of a C_{1-4} alkylene or C_{2-4} alkenylene group, for increasing the u.v. stability of a liquid crystal mixture.

As used herein the term "alkyl" refers to straight or branched chain alkyl groups, suitably containing up to 20, more suitably up to 10 and preferably up to 6 carbon atoms. The term "alkylene" refers to alkyl groups which are divalent and "cycloalkyl" refers to alkyl groups which have at least 3 carbon atoms, and which are cyclic in structure. The term "alkenyl" refers to straight or branched unsaturated chains having from 2 to 20 and preferably from 2 to 10 carbon atoms. The term "aryl" refers to aromatic rings such as phenyl and naphthyl, but preferably phenyl.

References to "heterocyclic groups" refer to rings, which suitably contain from 4 to 8 atoms, up to three of which are heteroatoms selected from oxygen, nitrogen or sulphur. They may be saturated or unsaturated, but are preferably saturated.

Suitably, rings in group A are para substituted, and where they are saturated, substituents are preferably in a trans relationship to each other. Particularly preferred examples of group A in formula (I) are groups of formula (i), (ii), (iii), (iv) or (v)



where X', X'' and X''' are each selected from a direct bond, a C₁₋₄alkylene chain or a C₂₋₄alkenylene chain, and each group R_a, R_b, R_c and R_d are independently selected from CH₂ or oxygen. In particular where one of R_a or R_b, or R_c or R_d is oxygen, the other is also oxygen so that the group A is or includes a dioxane ring.

In particular however, R_a, R_b, R_c and R_d, where present, are CH₂ groups.

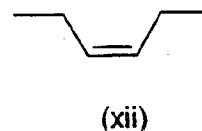
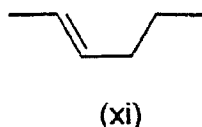
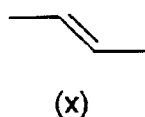
Suitably Y' and Y'' are oxygen.

In a particularly preferred embodiment, n is 2.

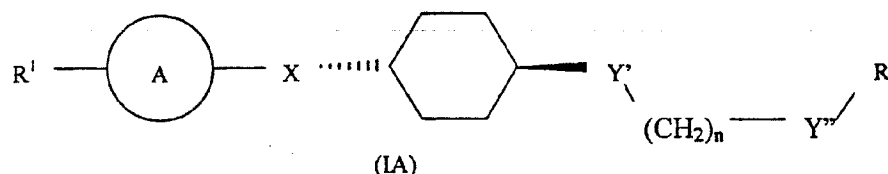
Suitably R² is a C₁₋₁₀alkyl, preferably C₁₋₆ alkyl and most preferably C₁₋₃alkyl. Alternatively, R² is alkyl having at least 5 carbon atoms, for example from 5 to 10 carbon atoms.

Preferably, X is a direct bond or a C₁₋₂alkylene chain, and most preferably X is a direct bond.

Where X is a C₂₋₄alkenylene chain, it is suitably a group of sub-formula (x), (xi) or (xii)

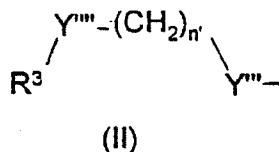


The cyclohexyl ring illustrated in Figure 1 is suitably in the trans configuration. Thus, in particular, the compound of formula (I) is suitably a compound of formula (IA)



where R^1 , R^2 , A, X, Y' , Y'' and n are as defined above.

In a preferred embodiment, R^1 is a straight chain C_{1-6} alkyl group and most preferably a C_{3-5} alkyl group, which optionally contains one or two oxygen or sulphur atoms. For example, a particular example of a group R^1 is a group of formula (II)

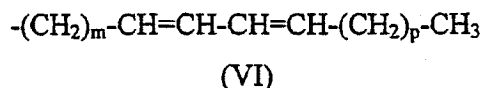


where n' is an integer from 1 to 5, Y''' and Y'''' are independently selected from oxygen or sulphur and R^3 is alkyl, in particular C_{1-4} alkyl. Preferably n' is 2. Preferably Y''' and Y'''' are oxygen.

Other particular examples of groups R^1 are C_{3-5} alkyl.

Yet further examples are C_{8-20} alkyl.

In an alternative embodiment, R^1 is an alkenyl group and in particular a C_{2-10} alkenyl group. Suitably the alkenyl group contains two or more double bonds, and is preferably a diene of formula (VI)

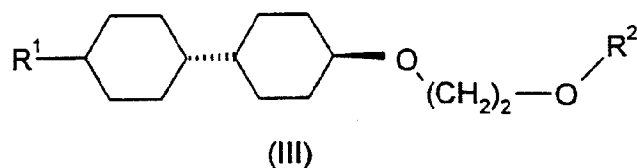


where m and p are 0 or an integer from 1-5, provided that $m+p$ does not exceed 5. Preferably m and p are 0.

Particularly suitable rings A in formula (I) are groups of sub-formula (i), (iii) and (v), and preferred rings A are groups of sub-formula (i). In groups of sub-formula (iii), (iv) and (v), X' , X'' and X''' are suitably direct bonds or C_{1-2} alkylene groups. Particularly, these are direct bonds. Where these are C_{2-4} alkenylene groups, these are suitably selected from groups (x), (xi) and (xii) as listed above in relation to X.

Thus particular examples of compounds of formula (I) are compounds of formula (III)

5



where R^1 and R^2 are as defined above.

Particular examples of compounds of formula (III) are set out in Table 1.

5

Table 1

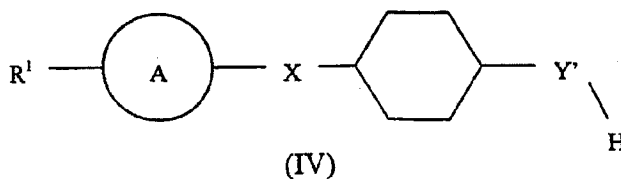
Compound No.	R^1	R^2
1	C_3H_7	CH_3
2	C_5H_{11}	CH_3
3	C_3H_7	C_2H_5
4	C_5H_{11}	C_2H_5
5	C_3H_5	C_3H_7

These compounds are suitably added to liquid crystal mixtures in order to increase the u.v. stability of those mixtures. Other components of the mixture will include liquid crystal compounds of various structures as are well known in the art.

- 10 Suitably the compound of formula (I) is added in sufficient quantities to produce a significant effect on the u.v. stability of the mixture. Therefore, the mixture will suitably contain the compound of formula (I) in an amount of from 5-80%, preferably from 5-40%, and most preferably from 10-30% by weight.

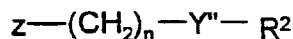
Compounds of formula (I) may be prepared by conventional methods.

- 15 However, in accordance with an aspect of the invention, they are prepared by reacting a compound of formula (IV)



20

where R^1 , A, X and Y' are as defined in relation to formula (I); with a compound of formula (V)



(V)

where Y'' and R² is as defined in relation to formula (I) and Z is a leaving group. The reaction is suitably effected in an organic solvent such as tetrahydrofuran in the presence of a strong base such as an alkali metal hydride for instance, sodium hydride. Suitable leaving groups Z include halo such as chloro, bromo or iodo, mesylate and tosylate, and in particular are halo groups such as bromo.

Compounds of formula (IV) are either known compounds or they can be prepared from known compounds by conventional methods.

Compounds of formula (I) have liquid crystal properties and in particular are nematic compounds. Thus they may be included in mixtures used in liquid crystal devices including liquid crystal display cells, such as twisted nematic cells (TN) (such as standard TN cells), supertwist nematic cells (STN) and supertwist birefringence effect (SBE) cells.

Such devices form a further aspect of the invention.

The compounds of formula (I) have good stability in the presence of radiation such as ultraviolet radiation. In particular they do not absorb radiation at the wavelengths used in many liquid crystal devices. These properties make them particularly useful, either alone or in mixture with other liquid crystal compounds, in liquid crystalline displays that are exposed to high levels of ultraviolet radiation, such as those used in outdoor displays. In addition, they may be utilized in conjunction with phosphorescent substrates or phosphor layer liquid crystal devices, such as those described in US Patent No. 4,830,469, WO 95/27920, EP-A-185495 and European Patent No 0755532.

These devices are particularly suitable for display cells and especially colour display cells as they overcome problems associated with the use of liquid crystals as shutters for transmitting light to a viewer. The light scattering or birefringent properties of these compounds is useful in this respect and may be controlled by application of an electrical field. However the liquid crystal material is sensitive to the angle at which light passes through it, and therefore there may be difficulties with viewing angle when these are viewed directly.

These problems are overcome in devices such as those mentioned above, by directing light from a light source, usually an ultraviolet light source, through the liquid crystal layer onto self-radiating elements or phosphors. These are activated by light reaching them through the liquid crystal layer, and thereafter emit light at a desirable viewing angle. Each phosphor therefore can constitute a pixel in a display or a combination of red, blue and green phosphors may be grouped to form a pixel which can emit light at any colour of the spectrum, depending upon the relative stimulation of each.

Thus a preferred liquid crystal device according to the invention is a display cell comprising a layer of a liquid crystal material wherein the liquid crystal material comprises a compound of formula (I), means for addressing the liquid crystal material so as to allow light to pass through it when appropriately addressed, and an emitting layer comprising phosphor elements, arranged to receive light passing through the liquid crystal layer.

Such devices are illustrated schematically in Figure 1 hereinafter. These devices may be arranged differently depending upon the intended application.

Suitably in these devices, the liquid crystal material is contained between two parallel, spatially separated transparent substrate plates (1), either in individual cells or in a continuous panel. Liquid crystal material (2), such as a compound of the present invention is provided in the cell, and the orientation is controllable by addressing means such as electrodes arranged on either side of the layer (not shown). Light from a light source is supplied in the direction of the arrow, and is either internally reflected by the liquid crystal material, or diverted to phosphors (3) on an emitting layer (4), depending upon the activation of the liquid crystal material. The phosphors may then emit light at a preferred viewing angle.

Devices may also contain polarisers and/or dichroic ultraviolet light absorbers (as described in US Patent No. 4,830,469).

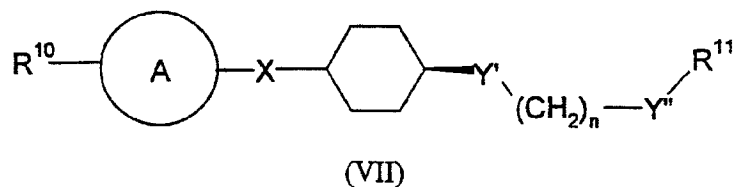
A particularly preferred device further comprises means for collimating activating light towards the phosphors. Various arrangements for such collimating means are described in WO 95/27920. They include lenses, which may be arranged in or on one of the layers.

Light from an ultra-violet light source, is supplied to the liquid crystal layer, either directly onto the back or from the edge using for example the transparent backing

plate as a light guide. The addressing means control the orientation of the liquid crystal material, within each cell or region of the panel as is well understood in the art. As a result, light may or may not be directed onto a particular phosphor element, which is either activated to emit light or remain dark, respectively. By appropriate control of the addressing means, each pixel point has individual visible light output characteristics at any given point in time.

Such devices may include computer or television screens, and these may contain hundreds of thousands of individual pixels, which control the amount of red, green or blue light reaching a very small area of the screen, for example of 100µm or less. In such cases, one of the electrodes used to address the liquid crystal material may be connected together in columns, and the other connected in rows (where rows and columns are perpendicular to each other) in order to reduce the number of electrical connections required. However, in order to ensure that pixels are controlled individually, these need to be multiplexed as understood in the art. Multiplexing generally achieved by applying a voltage which cycles between the desired voltage and zero many times per second. As each row receives the required voltage, a positive or negative voltage is applied to each column so that individual pixels within the row are addressed in the required manner. This means that the liquid crystal of all the "on" pixels will subject to a voltage in excess of the threshold voltage for that compound. All rows in the display are scanned to refresh the pixels.

Certain compounds of formula (I) are novel and these form a further aspect of the invention. In particular, the invention further provides a compound of formula (VII)

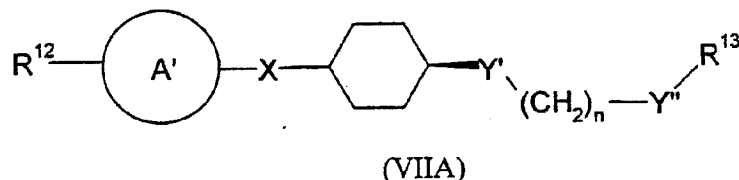


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wherein R^{10} is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R^{11} is an alkyl or alkenyl group, Y' , Y'' , n , X and A are as defined above in relation to formula (I) provided that when A is cycloalkyl, X is a direct bond or a C_2 alkylene chain, n is 2, Y' and Y'' are both oxygen, R^{11} is methyl, and R^{10} is an alkyl group, it contains more than 3 carbon atoms.

30

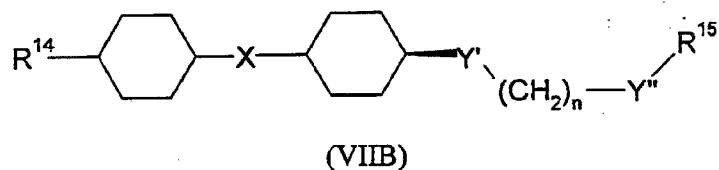
Particular groups of compounds of formula (VII) are compounds of formula (VIIA)



5 wherein R^{12} is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R^{13} is an alkyl or alkenyl group, Y' , Y'' , n , and X , and A is a group comprising one or two rings which are independently selected from aryl or heterocyclic, and when there are two rings, they are bonded together directly or by way of a C_{1-4} alkylene or C_{2-4} alkenylene group.

10 Preferred examples of R^{12} and R^{13} are as defined above in relation to R^1 and R^2 . Similarly preferred examples of X , Y' , Y'' and n are as defined above in relation to corresponding variables in formula (I). Preferred examples of A' are groups of sub-formula (ii), (iii), (iv) or (v) as defined above. Alternatively, A' may be a dioxane ring.

15 An alternative group of compounds of formula (VII) are compounds of formula (VIIB)



20 where X , Y' , Y'' and n are as defined above in relation to formula (I), R^{14} is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, and R^{15} is an alkyl or alkenyl group, provided that when R^{15} is methyl and R^{14} is alkyl of at least 4 and preferably at least 8 carbon atoms.

Suitably R^{14} is alkenyl.

More suitably R^{14} is alkyl of at least 4 and preferably at least 8 carbon atoms.

Suitably R^{15} is alkenyl

25 More suitably R^{15} is alkyl of at least 2 and preferably at least 5 carbon atoms.

Preferred variables for X , Y' , Y'' and n are as defined above in relation to formula (I).

Compounds of formula (VII), (VIIA) and (VIIB) may be prepared by conventional methods, for example by methods analogous to those described above in

relation to formula (I). These novel compounds have liquid crystal properties and therefore their use in liquid crystal devices, either alone or in admixture with other liquid crystal compounds forms a further aspect of the invention.

The invention will now be particularly described by way of example.

5

Example 1

Preparation of *trans, trans*-4'-(2-methoxyethoxy)-4-pentylbicyclohexane (Compound No. 2 in Table 1)

A solution of *trans*-4-(4-pentylcyclohexyl)-1-cyclohexanol (1.00 g, 3.97×10^{-3} mol) in
10 tetrahydrofuran (10 cm³) was added dropwise to a suspension of sodium hydride (0.14 g, 5.95×10^{-3} mol) in tetrahydrofuran (15 cm³) at room temperature and under a nitrogen atmosphere. The solution was then left to stir (2hrs) before 1-bromo-2-methoxyethane (0.83 g, 5.95×10^{-3} mol) and potassium iodide (0.07 g, 3.97×10^{-4} mol) were added dropwise and the reaction mixture then refluxed (48 hrs). Methanol (20 cm³) was then
15 added to the reaction mixture followed by water (75 cm³). The product was then extracted into ether (3 × 30cm³) and then the combined organic layers were washed with brine (2 × 20cm³) and dried over magnesium sulphate. The solution was then filtered and the solvent removed under reduced pressure and the crude product purified by column chromatography on silica gel using a 3:7 ethylacetate/hexane mixture as eluent
20 and recrystallised from cold propanone, producing the desired white crystalline product. Yield 0.44 g (36 %) GC purity (99.9 %).

Cr-I = 65 °C S_B-I = 64 °C

Example 2

25 Using analogous methods to that described in Example 1 but with different starting materials, the following compounds were prepared.

trans, trans-4'-(2-ethoxyethoxy)-4-pentylbicyclohexane (Compound 4 in Table 1)

Yield 0.43 g (33 %) GC purity (99.8 %).

30 Cr-I = 25 °C

trans, trans-4'-(2-methoxyethoxy)-4-propylbicyclohexane (Compound 1 in Table 1)

Yield 0.29 g (22 %) GC purity (100 %).

Cr-I = 47 °C N-I = 44 °C

5 trans, trans-4'-(2-ethoxyethoxy)-4-propylbicyclohexane (Compound 3 in Table 1)

Yield 0.15 g (11 %) GC purity (99.6 %).

Cr-I = 20 °C N-I = 7 °C

trans, trans-4'-(2-propoxyethoxy)-4-propylbicyclohexane (Compound 5 in Table 1)

Yield 0.08 g (12 %) GC purity (100%).

10 Cr-I = 90°C

Example 3

Liquid Crystal Properties

The liquid crystal properties of the compounds of the invention were tested using
15 conventional methods. In particular the melting and clearing points of compounds of the invention and structurally similar compounds were determined for comparison purposes. The results are shown in Tables 2-6.

Table 2 shows for the *trans, trans*-4-propyl,4'-R-bicyclohexyl core compound the effect
20 of the position and number of oxygen atoms incorporated in the 5 atom end chain. All members of the series except the ethyleneoxy derivative exhibit a smectic B phase. *Trans, trans*-4-propyl,4'-pentylbicyclohexane shows only a smectic B phase. This is also the behaviour when one of the carbons in the pentyl chain is replaced with an oxygen. When, however, two carbons are replaced as in the methyl ethyleneoxy
25 derivative Compound No 1, the smectic B phase is lost and a monotropic nematic phase is observed.

Table 3 shows for both the propyl and pentyl cyclohexyl analogues the effect of
extending the ethyleneoxy chain by 1 carbon unit at the terminus. Extending the
30 terminal chain by only 1 carbon atom has a very large effect on the melting point, which is substantially reduced in the C3 and C5 homologues Compounds 3 and 4 when compared with the shorter chain of Compounds 1 and 2.

Table 2



Compound No.	R	Cr	SmB	N	Iso Liq
Comparative Example A		• 23	• 96	-	•
Comparative Example B		• 32	• 74	-	•
Comparative Example C		• 15	• 42	-	•
Comparative Example D		• 25	• 85	-	•
Compound no 1		• 47	(• 44)		•

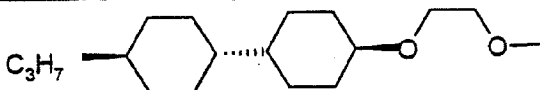
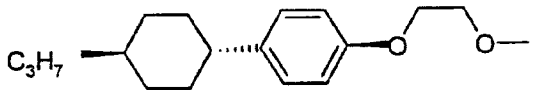
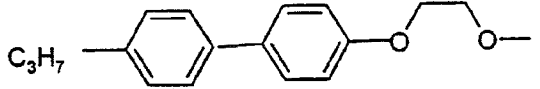
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Table 3

Compound No. (Table 1)	Cr	SmB	N	Iso Liq
1	• 47	•	(• 44)	•
3	• 20	•	(• 7)	•
2	• 65	(• 64)		•
4	• 25			•
5	• 90			•

Table 4 shows the effect of the ethyleneoxy end chain with a number of different cores. Replacement of the cyclohexyl group with a phenyl group in Comparative Example 1A leads to a reduction in the stability of the nematic phase, which remains a monotropic transition, as it does in the tolane. A nematic phase is not observed in the biphenyl derivative.

Table 4


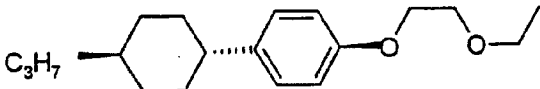
Compound No.	Structure	Cr	N	Iso	Liq	
Compound No 1		•	47	•	(44)	•
Comparative Example 1A		•	41	•	(13)	•
Comparative Example 1B		•	97			•

A similar trend in melting and clearing points was found in the pentyl derivatives.

- 5 Table 5 shows the same cores and end chain as Table 4 but here the ethyleneoxy chain is extended by 1 carbon unit, to terminate in an ethyl group instead of a methyl group. The overall trends are again dependant on the core, the melting points are however reduced. None of the compounds exhibit an enantiotropic nematic phase.

10

Table 5

Compound No.	Structure	Cr	N	Iso	
3		•	20	• (7)	•
Comparative Example 3		•	13	• (<-20)	•

In Table 6, the ethyleneoxy end chain is sequentially increased by 1 carbon unit from methoxy- to propyloxy- ethenyloxy- bicyclohexyl. The melting point falls and then rises substantially in a typical manner as the end chain is increased in length.

15

Table 6

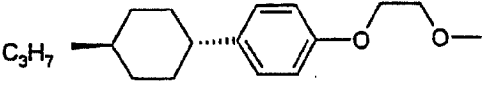
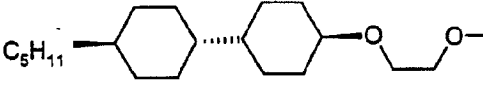
Compound No. (Table 1)	Cr	N	Iso Liq
1	• 47	• (44)	•
3	• 20	• (7)	•
5	• 90		•

Example 4Physical Properties

- 5 The physical properties of a number of the compounds described were evaluated using conventional methods.

The dipole moments of the two compounds Comparative Example 2 and Compound No 2 were determined from extrapolation in solution in PCH32 at 25°C at 4, 6, 8 and 10% concentrations measured in a 9 μ m cell. The dipole moments for the two compounds appear very similar and are shown in Table 7.

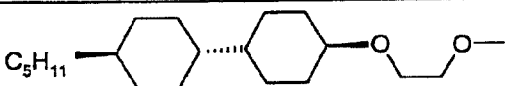
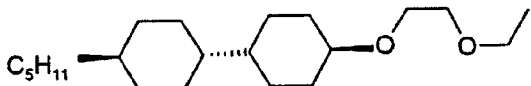
Table 7

Compound No.	Structure	μ (D)
Comparative Example 2		2.32
Compound No 2		2.26

15 Example 5Properties of Mixtures

- Mixtures of dicyclohexyl ethyleneoxy compounds in a standard basic mixture ethyl linked phenyl cyclohexanes were made and the phase behaviour, permittivities and birefringence determined. The mixtures, phase behaviour and structure of the compounds is listed in Table 8. None of the mixtures exhibited higher order smectic phases.

Table 8

Mixture number, % of compound	Compound No and transition temperatures	Structure	Clearing point of mixture (°C)
I 9.75%	2 K65(SmB 64)		49.9
II 9.94%	4 K27.2I		46.5

The permittivities of the mixtures are shown in Table 9.

Table 9

Mixture	$\epsilon_{\uparrow\uparrow}$	ϵ_{\perp}	$\Delta\epsilon$
I	11.8684	5.1236	6.75
II	11.6578	5.1522	6.51
Mixture ethyl linked phenyl cyclohexanes	12.95	5.13	7.82

5

The birefringence of the mixtures of 25°C and 30° below the clearing point of the mixture are given in Table 10. All mixtures show low birefringence.

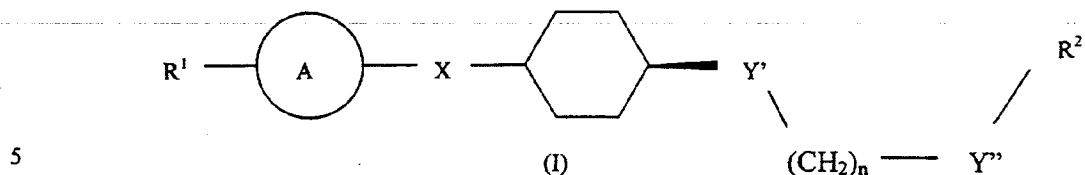
Table 10

Mixture	Temperature (°C)	n_e	n_o	Δn
I	25	1.5713	1.4833	0.088
	19.9	1.5755	1.4841	0.091
II	25	1.5683	1.4841	0.084
	16.5	1.5750	1.4853	0.0897

10

Claims

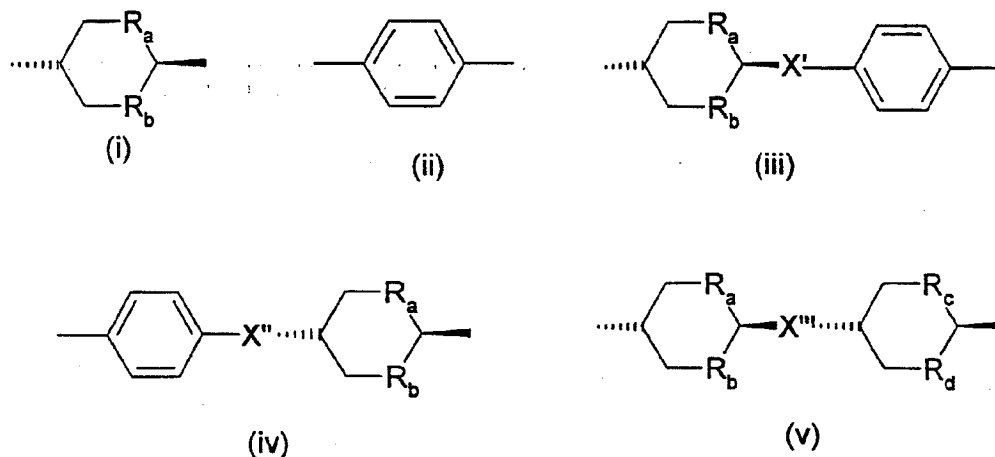
1. The use of a compound of formula (I)



wherein R^1 is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R^2 is an alkyl or alkenyl group, Y' and Y'' are independently selected from oxygen or sulphur, n is an integer from 1 to 5, X is a direct bond or a C_{1-4} alkylene or C_{2-4} alkenylene chain, and A is group comprising one or two rings which are independently selected from aryl, heterocyclic or cycloalkyl rings, and when there are two rings, they are bonded together directly or by way of a C_{1-4} alkylene or C_{2-4} alkenylene group, for increasing the u.v. stability of a liquid crystal mixture.

15

2. The use according to claim 1 wherein the group A in formula (I) is selected from a group of formula (i), (ii), (iii), (iv) or (v)



where X' , X'' and X''' are each selected from a direct bond, a C_{1-4} alkylene chain or a C_{2-4} alkenylene chain, and each group R_a , R_b , R_c and R_d are independently selected from CH_2 or oxygen.

3. The use according to claim 2 wherein R_a , R_b , R_c and R_d , where present, are CH_2 groups.
4. The use according to any one of the preceding claims wherein Y' and Y'' in
5 formula (I) are oxygen.
5. The use according to any one of the preceding claims wherein n in formula (I) is 2.
- 10 6. The use according to any one of the preceding claims wherein R^2 in formula (I) is a C_{1-10} alkyl.
7. The use according to claim 6 wherein R^2 in formula (I) is C_{1-3} alkyl.
- 15 8. The use compound according to any one of the preceding claims wherein X in formula (I) is a direct bond or a C_{1-2} alkylene chain.
9. The use according to claim 8 wherein X in formula (I) is a direct bond.
- 20 10. The use according to any one of claims 1 to 7 wherein X is a C_{2-4} alkenylene chain of formula (x), (xi) or (xii)



(x)

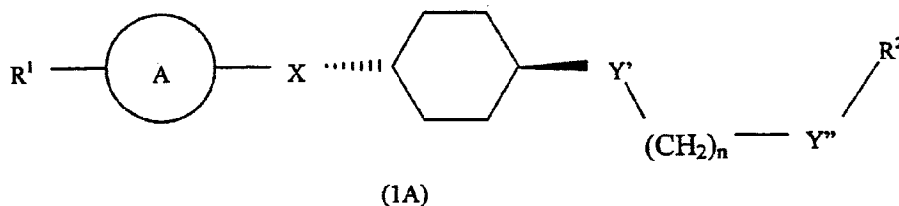


(xi)



(xii)

11. The use according to any one of the preceding claims wherein the compound of
25 formula (I) is a compound of formula (IA)



where R^1 , R^2 , A , X , Y' , Y'' and n are as defined in claim 1.

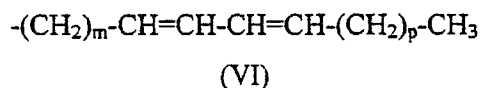
12. The use according to any one of the preceding claims wherein R^1 in formula (I) is a straight chain C_{1-6} alkyl group which optionally contains one or two oxygen or sulphur atoms.

13. The use according to any one of claims 1 to 11 wherein R^1 in formula (I) is a C_{2-10} alkenyl group.

14. The use according to claim 13 wherein the alkenyl group R^1 contains two double bonds.

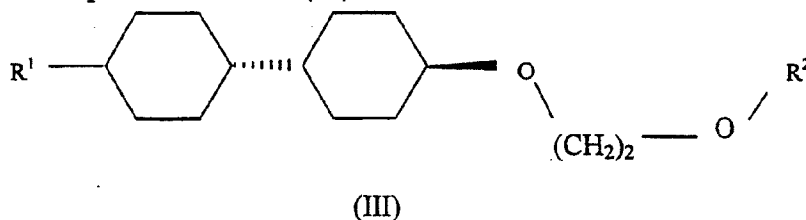
10

15. The use according to claim 14 wherein the alkenyl group R^1 is a diene of formula (VI)



16. where m and p are 0 or an integer from 1-5, provided that $m+p$ does not exceed 5.

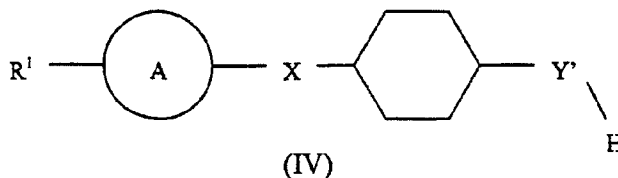
17. The use according to any one of the preceding claims wherein the compound of formula (I) is a compound of formula (III)



20

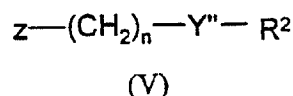
where R^1 and R^2 are as defined in claim 1.

18. A method for preparing a compound of formula (I) as defined in any one of the preceding claims which comprises reacting a compound of formula (IV)



30

where R^1 , A, X and Y' are as defined in relation to formula (I) in claim 1; with a compound of formula (V)



5 where Y'' and R^2 is as defined in claim 1 and Z is a leaving group.

18. A liquid crystal device comprising an outdoor liquid crystal display device, or a device comprising a phosphorescent substrate or a phosphor layer, said device comprising a compound of formula (I) as defined in any one of claims 1 to 16.

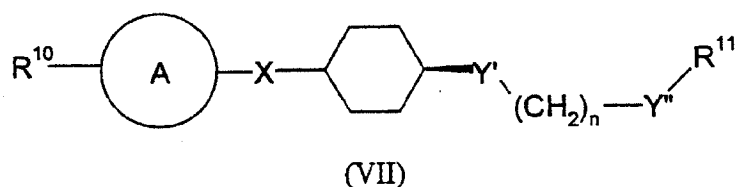
10

19. A liquid crystal device according to claim 18 wherein the compound of formula (I) is in admixture with other liquid crystal compounds.

20. A liquid crystal device which comprises a display cell comprising a layer of a liquid crystal material wherein the liquid crystal material comprises a compound of formula (I) as defined in claim 1, means for addressing the liquid crystal material so as to allow light to pass through it when appropriately addressed, and an emitting layer comprising phosphor elements, arranged to receive light passing through the liquid crystal layer.

20

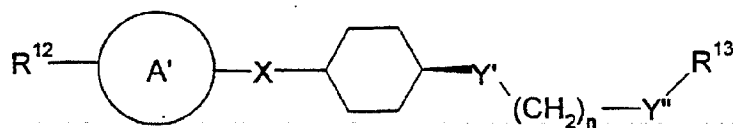
21. A compound of formula (VII)



25 wherein R^{10} is an alkyl or alkenyl group, either of which may be optionally interposed with one or more oxygen or sulphur atoms, R^{11} is an alkyl or alkenyl group, Y' , Y'' , n, X and A are as defined in claim 1, provided that when A is cycloalkyl, X is a direct bond or a C_2 alkylene chain, n is 2, Y' and Y'' are both oxygen, R^{11} is methyl, and R^{10} is an alkyl group, it contains more than 3 carbon atoms.

30

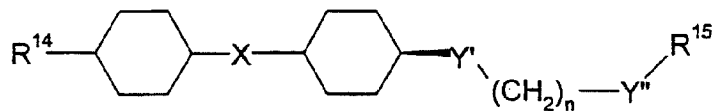
22. A compound according to claim 21 of formula (VIIA)



(VIIA)

wherein R^{12} is an alkyl or alkenyl group, either of which may be optionally interposed
 5 with one or more oxygen or sulphur atoms, R^{13} is an alkyl or alkenyl group, Y' , Y'' , n ,
 and X are as defined in claim 1, and A is a group comprising one or two rings which
 are independently selected from aryl or heterocyclic, and when there are two rings, they
 are bonded together directly or by way of a C_{1-4} alkylene or C_{2-4} alkenylene group.

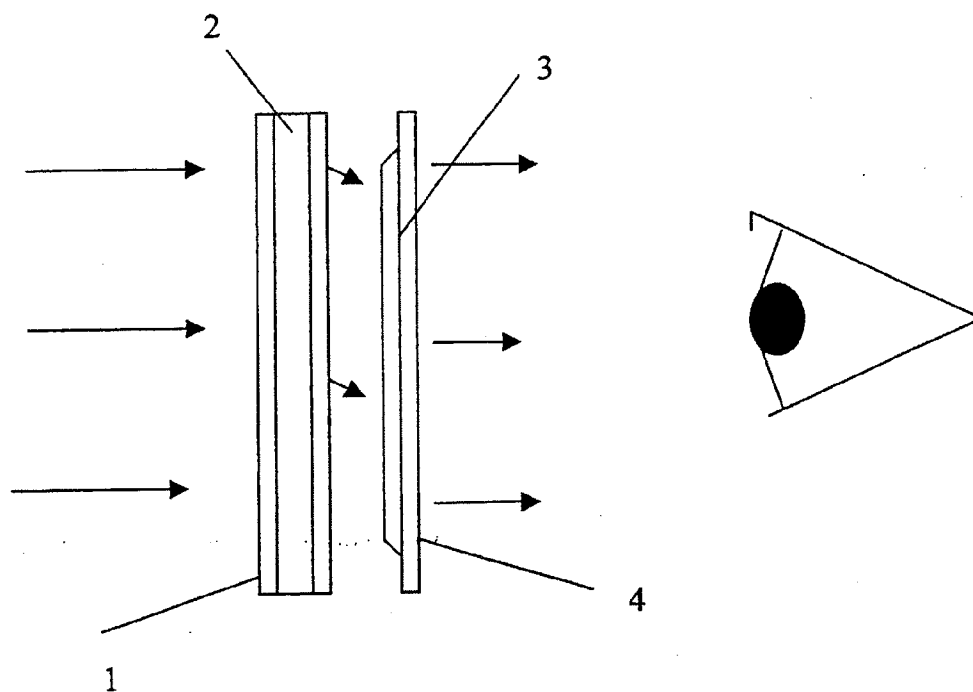
10 23. A compound according to claim 21 of formula (VIIB)



(VIIB)

where X , Y' , Y'' and n are as defined in claim 1, R^{14} is an alkyl or alkenyl group, either
 of which may be optionally interposed with one or more oxygen or sulphur atoms, and
 15 R^{15} is an alkyl or alkenyl group, provided that when R^{15} is methyl and R^{14} is alkyl of at
 least 4.

Fig.1.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/03165

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K19/30 C07C43/184 C09K19/34 G02F1/13357

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C07C G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 132 553 A (MERCK PATENT GMBH ;SECR DEFENCE BRIT (GB)) 13 February 1985 (1985-02-13)	21-23
Y	page 4, line 4 - line 22; claims ---	1-20
Y	WO 93 02152 A (MERCK PATENT GMBH) 4 February 1993 (1993-02-04) page 5, line 20 - line 31 page 7; claims ---	1-20
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 205 (C-595), 15 May 1989 (1989-05-15) & JP 01 022835 A (DAINIPPON INK & CHEM INC), 25 January 1989 (1989-01-25) cited in the application	21-23
Y	abstract --- -/--	1,11,16

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Date of the actual completion of the international search

25 October 2002

Date of mailing of the international search report

11 OCTOBER 2002

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Serbetsoglou, A

INTERNATIONAL SEARCH REPORT

Intern Application No

PCT/GB 02/03165

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 385 471 A (DAINIPPON INK & CHEMICALS) 5 September 1990 (1990-09-05) cited in the application claims ---	1-23
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 392 (C-0873), 4 October 1991 (1991-10-04) & JP 03 161453 A (DAINIPPON INK & CHEM INC), 11 July 1991 (1991-07-11) abstract ---	1-17, 21-23
A	EP 0 315 050 A (HOFFMANN LA ROCHE) 10 May 1989 (1989-05-10) page 9 -page 12; claims ---	1-23
A	US 5 746 940 A (COATES DAVID ET AL) 5 May 1998 (1998-05-05) column 1, line 1 -column 3, line 43; claims 1-5,12 ---	1-23
A	WO 87 07266 A (MERCK PATENT GMBH) 3 December 1987 (1987-12-03) page 4, line 20 -page 6, line 5; claims ---	1,21
A	KELLY S M: "THE SYNTHESIS AND LIQUID CRYSTAL TRANSITION TEMPERATURES OF SOME WEAKLY POLAR NEMATIC TRANS-4-SUBSTITUTED-CYCLOHEXYL (E)-ALK-2- ENOATES" LIQUID CRYSTALS, TAYLOR AND FRANCIS LTD, LONDON, GB, vol. 17, no. 2, 1 August 1994 (1994-08-01), pages 211-225, XP000460892 ISSN: 0267-8292 tables 1,6 ---	1-16, 21-23
A	SCHADT M ET AL: "MATERIAL PROPERTIES, STRUCTURAL RELATIONS WITH MOLECULAR ENSEMBLES AND ELECTRO-OPTICAL PERFORMANCE OF NEW BICYCLOHEXANE LIQUID CRYSTALS IN FIELD-EFFECT LIQUID CRYSTAL DISPLAYS" LIQUID CRYSTALS, BASINGSTOKE, HAMPSHIRE, GB, vol. 5, no. 1, 1989, pages 293-312, XP000210415 table 2 ---	1-16, 21-23
A	WO 90 04622 A (MERCK PATENT GMBH) 3 May 1990 (1990-05-03) claims; examples 1,4-6,9,10 ---	1-16, 21-23

-/--

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/GB 02/03165

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 830 469 A (BREDEL PAULUS A ET AL) 16 May 1989 (1989-05-16) cited in the application claims	18-20
A	WO 95 27920 A (CROSSLAND WILLIAM ALDEN; DIXON ALAN COLIN; THOMAS JOHN) 19 October 1995 (1995-10-19) cited in the application claims	18-20

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/GB 02/03165

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0132553	A	13-02-1985	DE 3321373 A1	20-12-1984
			DE 3348305 C2	17-06-1992
			DE 3469294 D1	17-03-1988
			EP 0132553 A1	13-02-1985
			HK 103988 A	30-12-1988
			JP 1822352 C	10-02-1994
			JP 5020418 B	19-03-1993
			JP 60016940 A	28-01-1985
			JP 6025669 A	01-02-1994
			JP 7108976 B	22-11-1995
			US 4622164 A	11-11-1986
			US 4868341 A	19-09-1989
WO 9302152	A	04-02-1993	DE 4123389 A1	21-01-1993
			DE 59209379 D1	23-07-1998
			WO 9302152 A1	04-02-1993
			EP 0548318 A1	30-06-1993
JP 01022835	A	25-01-1989	NONE	
EP 0385471	A	05-09-1990	JP 2229127 A	11-09-1990
			JP 2701426 B2	21-01-1998
			JP 2229129 A	11-09-1990
			JP 2701427 B2	21-01-1998
			JP 2233635 A	17-09-1990
			JP 2782762 B2	06-08-1998
			JP 2255636 A	16-10-1990
			JP 2701439 B2	21-01-1998
			JP 2273638 A	08-11-1990
			JP 2311441 A	27-12-1990
			JP 2715549 B2	18-02-1998
			JP 2715554 B2	18-02-1998
			JP 3017038 A	25-01-1991
			DE 69002775 D1	23-09-1993
			DE 69002775 T2	05-01-1994
			EP 0385471 A1	05-09-1990
			HK 1005313 A1	31-12-1998
			US 5178794 A	12-01-1993
JP 03161453	A	11-07-1991	NONE	
EP 0315050	A	10-05-1989	DE 3883705 D1	07-10-1993
			EP 0315050 A2	10-05-1989
			HK 33195 A	17-03-1995
			JP 1151531 A	14-06-1989
			JP 2693525 B2	24-12-1997
			KR 214791 B1	02-08-1999
			SG 181194 G	12-05-1995
			US 5013477 A	07-05-1991
US 5746940	A	05-05-1998	GB 2297556 A	07-08-1996
			JP 8239666 A	17-09-1996
WO 8707266	A	03-12-1987	DE 3617431 A1	26-11-1987
			WO 8707266 A2	03-12-1987
			EP 0270580 A1	15-06-1988
WO 9004622	A	03-05-1990	DE 3835804 A1	26-04-1990

INTERNATIONAL SEARCH REPORT

Intern	Application No
PCT/GB	02/03165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9004622	A	AT 113308 T	15-11-1994
		CA 2000926 A1	20-04-1990
		CN 1042173 A	16-05-1990
		DD 288613 A5	04-04-1991
		DE 58908566 D1	01-12-1994
		WO 9004622 A1	03-05-1990
		EP 0366985 A1	09-05-1990
		EP 0394417 A1	31-10-1990
		ES 2063095 T3	01-01-1995
		HK 69195 A	12-05-1995
		JP 2709859 B2	04-02-1998
		JP 3504139 T	12-09-1991
		KR 153124 B1	02-11-1998
		SG 37095 G	01-09-1995
		US 6210760 B1	03-04-2001
		US 5876626 A	02-03-1999
		US 5387369 A	07-02-1995
US 4830469	A 16-05-1989	DE 8801498 U1	26-05-1988
		EP 0282109 A1	14-09-1988
		JP 63216029 A	08-09-1988
WO 9527920	A 19-10-1995	AU 2112195 A	30-10-1995
		BR 9507295 A	30-09-1997
		CA 2187156 A1	19-10-1995
		DE 69506240 D1	07-01-1999
		DE 69506240 T2	22-04-1999
		EP 0755532 A1	29-01-1997
		WO 9527920 A1	19-10-1995
		GB 2301928 A ,B	18-12-1996
		HK 1011417 A1	28-04-2000
		IL 113286 A	08-02-1998
		JP 9511588 T	18-11-1997
		ZA 9502852 A	04-01-1996